The nature of the chemical bonding in 5d transition-metal diatomic borides MB (M = Ir, Pt, Au)

Cite as: J. Chem. Phys. **152**, 174301 (2020); https://doi.org/10.1063/5.0008484 Submitted: 24 March 2020 . Accepted: 13 April 2020 . Published Online: 01 May 2020

Ling Fung Cheung ២, G. Stephen Kocheril ២, Joseph Czekner, and Lai-Sheng Wang ២



ARTICLES YOU MAY BE INTERESTED IN

Low energy electron impact resonances of anthracene probed by 2D photoelectron imaging of its radical anion

The Journal of Chemical Physics **152**, 174303 (2020); https://doi.org/10.1063/5.0007470

NWChem: Past, present, and future The Journal of Chemical Physics 152, 184102 (2020); https://doi.org/10.1063/5.0004997

Essentials of relativistic quantum chemistry The Journal of Chemical Physics 152, 180901 (2020); https://doi.org/10.1063/5.0008432





J. Chem. Phys. **152**, 174301 (2020); https://doi.org/10.1063/5.0008484 © 2020 Author(s).

The nature of the chemical bonding in 5d transition-metal diatomic borides MB (M = Ir, Pt, Au)

Cite as: J. Chem. Phys. 152, 174301 (2020); doi: 10.1063/5.0008484 Submitted: 24 March 2020 • Accepted: 13 April 2020 • Published Online: 1 May 2020 Ling Fung Cheung, ⓑ C. Stephen Kocheril, ⓑ Joseph Czekner, ⓑ and Lai-Sheng Wang^a) ⓑ AFFILIATIONS

Department of Chemistry, Brown University, 324 Brook Street, Providence, Rhode Island 02912, USA

^{a)}Author to whom correspondence should be addressed: lai-sheng_wang@brown.edu

ABSTRACT

Boron can form strong bonds with transition metals in diatomic metal borides (MB), but the nature of the chemical bonding has not been well understood. Recently, a quadruple bond was discovered in Rh \equiv B, consisting of two σ bonds formed between the Rh 4d_{z²} and B 2s/2p orbitals and two π bonds between the Rh 4d_{zz}/4d_{yz} and the B 2p_x/2p_y orbitals. The bonding between the 5d transition metals and boron is expected to be even stronger. Here, we report an investigation on the electronic structure and chemical bonding of the 5d transition metal diatomic borides (IrB, PtB, and AuB) using high-resolution photoelectron imaging on the corresponding anions (MB⁻) and theoretical calculations. Vibrationally resolved photoelectron spectra are obtained for all three anions, and the electron affinities are measured for IrB, PtB, and AuB to be 1.995(1), 2.153(3), and 0.877(6) eV, respectively. It is found that the weakly anti-bonding 3 σ molecular orbital (mainly of M 6s and B sp characters) is singly occupied in IrB (³ Δ) and PtB (² Σ ⁺), resulting in a bond order of three and half for these two diatomic borides. The 3 σ orbital is doubly occupied in AuB (¹ Σ ⁺), giving rise to a weak triple bond. Despite the lower bond order, the bonding in IrB and PtB is only slightly weaker than that in RhB due to the more favorable interactions between the M 5d orbitals and the B sp orbitals.

Published under license by AIP Publishing. https://doi.org/10.1063/5.0008484

I. INTRODUCTION

Transition metal borides (MB) have become an active area of investigation to search for ultrahard materials due to the strong covalent bonding between transition metals and boron, ^{1–3} particularly for 4d and 5d transition metals. The nature of the chemical bonding between a metal and boron plays a central role in determining the hardness of a given transition metal boride material among other factors.^{4,5} However, there have been limited previous experimental and theoretical investigations, and the nature of the chemical bonding has not been well understood even for the simplest diatomic transition-metal borides (MB).^{6–25} In a very recent study, we have found serendipitously that rhodium and boron can form a quadruple bond in the diatomic RhB (Rh \equiv B), the first experimentally confirmed quadruple bond in a diatomic species involving B.²⁶

The valence molecular orbital (MO) diagram for RhB, along with the orbital compositions, is reproduced in Fig. 1 for the convenience of discussion. The quadruple bond in Rh \equiv B consists of two

 σ bonds formed between the Rh 4d₂ and B 2s/2p orbitals and two π bonds between the Rh 4d_{xz}/4d_{yz} and the B 2p_x/2p_y orbitals. The 1σ MO was viewed as a B 2s lone pair previously, 10,11,25 which is generally true for 3d diatomic borides,¹² but it clearly has a significant contribution from the $4d_{a^2}$ orbital of Rh (Fig. 1). The covalent bonding nature of the 1σ MO was further confirmed by considering RhBH⁺, in which the 1 σ orbital is "destroyed" by forming the B–H bond.²⁶ It was shown that the Rh–B bond in RhBH⁺ is weakened and reduced to a triple bond $[Rh \equiv B-H]^+$. The quadruple bond in Rh≣B is corroborated by the fact that its bond dissociation energy (D_0) is the largest (5.252 eV) among a series of late transition metal MB species reported recently, including 3d, 4d, and 5d transition metals.²⁵ The bonding between the 5d transition metal and boron is expected to be stronger. Surprisingly, the D_0 of the isoelectronic IrB (4.928 eV) is lower than that of RhB, whereas that of PtB (5.235 eV) is the second largest among the late transition metal diatomic species.⁴

To probe the electronic structure and elucidate the bonding in IrB and PtB, we have carried out a high resolution photoelectron



FIG. 1. The MO diagram and atomic compositions for Rh≣B from Ref. 26.

imaging study of their anions in conjunction with theoretical calculations. We have also investigated the AuB diatomic species for comparison. Spectroscopically, there was relatively little known about these species. Laser-induced fluorescence (LIF) spectroscopy was reported for IrB, and its ground state was deduced to be ${}^{3}\Delta_{3}$ with a vibrational frequency of 909.63 cm⁻¹ (${}^{193}Ir^{11}B$) and 909.92 cm⁻¹ (${}^{191}Ir^{11}B$).^{13,18} There was also one LIF spectroscopy study on PtB, which was found to have a ${}^{2}\Sigma^{+}$ ground state and a vibrational frequency of 903.60 cm⁻¹ (Pt¹¹B).²⁰ There were no previous spectroscopy studies on AuB, except an early Knudsen cell experiment yielding a dissociation energy of 3.77 eV.⁶

We have been interested in the electronic structure and chemical bonding in size-selected boron and metal-doped boron clusters using photoelectron spectroscopy (PES) and computational chemistry.4 ⁶ It has been shown that PES is a powerful experimental technique to probe the electronic structure and bonding of novel cluster species. Here, we report a high-resolution photoelectron (PE) imaging and theoretical study of IrB⁻, PtB⁻, and AuB⁻. Vibrationally resolved PE spectra are obtained for all three anions, and the electron affinities are measured for IrB, PtB, and AuB to be 1.995(1), 2.153(3), and 0.877(6) eV, respectively, for the first time. In addition to the ground state $({}^{3}\Delta_{3})$ of IrB, the ${}^{3}\Delta_{2}$ and $^{1}\Delta_{2}$ excited states are also observed, whereas only the ground electronic states are observed for PtB and AuB. Vibrational frequencies are obtained for the ground states of IrB (${}^{3}\Delta_{3}$), PtB (${}^{2}\Sigma^{+}$), and AuB (${}^{1}\Sigma^{+}$): 925(8) cm⁻¹ for ¹⁹³Ir¹¹B, 974(27) cm⁻¹ for ¹⁹⁵Pt¹⁰B, and 704(26) cm⁻¹ for Au¹⁰B. It is found that the weakly antibonding 30 molecular orbital (mainly of M 6s and B sp characters) is singly occupied in IrB (³ Δ) and PtB (² Σ ⁺), resulting in a bond order of three and half for these two diatomic borides. The 3σ orbital is doubly occupied in AuB ($^1\Sigma^+$), giving rise to a weak triple bond.

II. EXPERIMENTAL METHODS

The experiments were conducted using a high-resolution PE imaging apparatus, which has been described in detail previously.³⁷ Briefly, the second harmonic of a Nd:YAG laser was focused onto a disk target pressed using a mixture of the metal (Ir, Pt, or Au), isotopically enriched ¹⁰B or ¹¹B, and silver powders at room temperature. The silver powder was added as a binder and allowed robust targets to be produced by cold-press. The laser-induced plasma was cooled by a helium carrier gas seeded with 10% argon, initiating nucleation. The nascent clusters were entrained by the carrier gas and underwent a supersonic expansion, producing a cold cluster beam. Anionic clusters were extracted perpendicularly into a time-of-flight mass spectrometer. The MB⁻ species of interest were mass selected before entering the interaction zone of the velocitymap imaging (VMI) analyzer. Diatomic anionic species were more challenging to produce in our cluster source, which favored the production of larger clusters.³¹ Significant anionic intensities for diatomic species were observed usually not under the best cooling conditions.

A second laser beam from a Nd:YAG laser or a Deyang Tech dye laser was used to photodetach electrons from the size-selected anions. Photoelectrons were focused onto a set of microchannel plates coupled with a phosphor screen and a charge-coupled-device camera. A typical experiment at a given photon energy required about 50 000–200 000 laser shots to achieve reasonable signal-tonoise ratios. The VMI lens was calibrated using the PE images of Au⁻ and Bi⁻ at various photon energies. The PE images were analyzed using the maximum entropy method (MEVELER).³⁹ The typical energy resolution of the VMI detector was ~0.6% for high kinetic energy electrons and as low as 1.2 cm⁻¹ for low kinetic energy electrons.³⁷

Photoelectron angular distributions (PADs) were obtained from the PE images, which can be characterized by using an anisotropy parameter (β). The differential cross section of the photoelectrons can be expressed as

$$d\sigma/d\Omega = \sigma_{\rm Tot}/4\pi [1 + \beta P_2(\cos\theta)], \qquad (1)$$

where σ_{Tot} is the total cross section, P₂ is the second-order Legendre polynomial, and θ is the angle of the photoelectron relative to the laser polarization. Hence, the PAD is described by

$$I(\theta) \sim [1 + \beta P_2(\cos \theta)], \qquad (2)$$

where β has a value ranging from -1 to 2. This model works well for single photon transitions from randomly oriented particles. Because photons carry one unit of angular momentum ($l = \pm 1$), the outgoing photoelectrons have the same change in angular momentum. If an electron is detached from an *s* atomic orbital (l = 0), the outgoing photoelectron will have l = 1 (pure *p*-wave) with $\beta = 2$. It is nontrivial to interpret the β value for ionization from an MO since MOs are linear combinations of atomic orbitals. Nevertheless, the values of β can be used to qualitatively assess the symmetries of the molecular orbitals involved in the photodetachment process and discern different electronic transitions.⁴⁰

III. THEORETICAL METHODS

We performed geometric optimizations and vibrational analyses using the doubly hybrid B2PLYP functional with the aug-ccpVQZ basis set for B and the aug-cc-pVQZ-pp basis set with the relativistic pseudopotentials (ECP60MDF) for Ir, Pt, and Au.⁴¹⁻⁴⁵ Calculations for the excited states of IrB were done at the TD-B3LYP and multireference configuration interaction (MRCI) levels of theory.⁴ Bond dissociation energies were calculated at the coupled-cluster single double triple [CCSD(T)] level of theory. All calculations were done using the Gaussian 09 package except the MRCI calculation that was done using Molpro.^{47,48} The adiabatic detachment energy (ADE) for the ground state transition was calculated as the energy difference between the ground states of the optimized anion and neutral with zero-point energy corrections, and it also represents the electron affinity (EA) for the neutral molecule. Orbital composition analyses were done using the natural atomic orbital (NAO) method using Multiwfn 3.7.4

IV. EXPERIMENTAL RESULTS

A. IrB⁻

The PE images and spectra for IrB^- are presented in Fig. 2 at six photon energies from 1.9662 eV [Fig. 2(a)] to 2.5188 eV [Fig. 2(f)]. Four main peaks were observed, and they are labeled X, A, a, and B. The sharp peak X in Fig. 2(b) defines the EA of IrB to be 1.995 \pm 0.001 eV. The relative intensities and separations between these

J. Chem. Phys. **152**, 174301 (2020); doi: 10.1063/5.0008484 Published under license by AIP Publishing



FIG. 2. Photoelectron images and spectra of IrB^- at six photon energies: (a) 1.9662 eV, (b) 2.0416 eV, (c) 2.1354 eV, (d) 2.3305 eV, (e) 2.4074 eV, and (f) 2.5188 eV. The double arrow below the images indicates the laser polarization. The vertical lines represent vibrational progressions.

peaks suggest that they do not belong to a simple vibrational progression. Weak peaks due to vibrational hot bands were observed in the lower binding energy region below peak X, and they are labeled *hb*1, *hb*2, and *hb*3. A shoulder peak labeled *x* was observed on the lower binding energy side of peak A [Fig. 2(c)]. In addition, a weak peak was observed on the higher binding energy side of peaks X [Fig. 2(b)], A [Fig. 2(c)], and *a* [Fig. 2(d)], labeled *hb*4, *hb*5, and *hb*6, respectively. Finally, a weak peak *b* was observed at the high binding energy side [Fig. 2(f)] although this assignment was tentative because the signals were weak in the higher binding energy part of the spectrum. The binding energies of the observed peaks and their assignments are given in Table I and will be discussed in Sec. VI A. The PADs for peaks X, A, and B were examined, and the obtained β values at different electron kinetic energies are presented in Fig. 3.

B. PtB⁻

Figure 4 displays the PE images and spectra of PtB⁻ at three photon energies from 2.1937 eV [Fig. 4(a)] to 2.4810 eV [Fig. 4(c)]. The most intense peak (X) denotes the 0–0 transition and defines the EA for PtB to be 2.153 \pm 0.003 eV. A short vibrational

Band	BE	State	Energy shift relative to peak X	Energy shift relative to the 0–0 transitions	Assignment	BE (Theo.)	Freq. (Theo.)
hb1	1.788(4)	$^{3}\Delta_{3}$	-1672(15)	-1672(15)	12^{0}		
hb2	1.891(2)	$^{3}\Delta_{3}$	-840(9)	-840(9)	1_1^{0}		882
hb3	1.899(2)	$^{3}\Delta_{3}$	-778(9)	-778(9)	1_2^{1}		
Х	1.995(1)	$^{3}\Delta_{3}$	0	0	0_0^{0}	1.957	
hb4	2.011(1)	$^{1}\Delta$	131(5)	-847(5)	1_1^{0}		882
Χ	2.110(2)	$^{3}\Delta_{3}$	925(8)	925(8)	10^{1}		942
А	2.116(1)	$^{1}\Delta$	976(6)	0	0_0^{0}	$2.188^{a}/2.240^{b}$	
hb5	2.125(1)	$^{1}\Delta$	1050(6)	73(6)	1_1^{1}		
а	2.232(2)	$^{1}\Delta$	1908(9)	931(9)	1_0^{1}		
hb6	2.242(2)	$^{1}\Delta$	1996(9)	1013(9)	1_1^2		
В	2.355(2)	$^{3}\Delta_{2}$	2900(8)	0	0_0^{0}	2.382 ^b	
b	2.466(11)	$^{3}\Delta_{2}$	3795(45)	894(45)	1_0^{-1}		942

TABLE I. The experimental binding energies (BE) in eV and assignments of the observed peaks in the PE spectra of ¹⁹³ Ir¹¹B⁻. The energy shifts (cm⁻¹) relative to peak X and their corresponding 0–0 transitions are also given. The calculated BE (eV) and vibrational frequencies (cm⁻¹) are also given for comparison.

^a Calculated at the TD-B3LYP level using $^{3}\Delta$ state's geometry, but the vibrational frequency of the $^{1}\Delta$ state could not be computed at the current level of theory.

^bCalculated at the MRCI+SO level, with all valence orbitals and electrons included in the active space.

progression (peaks *a* and *b*) was observed, as denoted by the vertical lines in Figs. 4(b) and 4(c), yielding a vibrational frequency for the ground state of ¹⁹⁵Pt¹⁰B to be 974 ± 27 cm⁻¹. The sharp peak near the threshold in Fig. 4(c) with a binding energy of 2.461(3) eV could not be assigned to a detachment transition from PtB⁻, and it could be due to an impurity. A weak peak labeled *hb*1 was observed at the lower binding energy side of X, which should be due to a vibrational hot band of PtB⁻. The β values for the 0–0 transition obtained from the PADs at three electron kinetic energies are also displayed in Fig. 3. The binding energies of the observed vibrational peaks are given in Table II.

C. AuB⁻

The AuB⁻ anion was found to have a relatively low electron binding energy. Its PE image (Fig. 5) was measured at 1.4058 eV, which was already near the cutoff of our dye laser at the long wavelength side. In addition, the ion intensity of AuB⁻ was relatively



FIG. 3. The anisotropy parameters (β) of peaks X, A, B, C, and D in the photoelectron spectra of IrB⁻ and peak X in the photoelectron spectra of PtB⁻ and AuB⁻ at different electron kinetic energies.

weak from our cluster source. Both the low detachment laser flux and the low ion intensity gave rise to a spectrum with relatively poor signal-to-noise ratios even with a long averaging time. The most intense peak (X) denotes the 0–0 transition and defines the



FIG. 4. Photoelectron images and spectra of PtB⁻ at three photon energies: (a) 2.1937 eV, (b) 2.3305 eV, and (c) 2.4810 eV. The double arrow below the images indicates the laser polarization. The vertical lines represent vibrational structures.

TABLE II. The experimental binding energies (BE) in eV of the observed vibrational peaks in the PE spectra of 195 Pt¹⁰B⁻ and Au¹⁰B⁻. The energy shift (in cm⁻¹) relative to peak X is also given. The calculated BE (eV) and vibrational frequencies (cm⁻¹) are given for comparison.

Band	BE	State	Energy shift relative to peak X	BE (Theo.)	Freq. (Theo.)
			¹⁹⁵ Pt ¹⁰ B ⁻		
hb1	2.050(6)	$^{2}\Sigma^{+}$	-829(32)		913
Х	2.153(3)	$^{2}\Sigma^{+}$	0	2.097	
a	2.274(4)	$^{2}\Sigma^{+}$	974(27)		984
b	2.392(5)	$^{2}\Sigma^{+}$	1932(30)		
			$Au^{10}B^-$		
x	0.877(6)	$^{1}\Sigma^{+}$	0	0.764	
a	0.964(4)	$^{1}\Sigma^{+}$	704(26)		710
b	1.049(5)	${}^{1}\Sigma^{+}$	1383(30)		

EA of AuB to be 0.877 \pm 0.006 eV. A short vibrational progression (peaks *a* and *b*) was discernible, yielding a vibrational frequency for Au¹⁰B to be 704 \pm 26 cm⁻¹. The β value obtained from the PAD of peak X is also shown in Fig. 3. The binding energies of the observed vibrational peaks are also given in Table II.

V. THEORETICAL RESULTS

A. IrB⁻

The electron configuration for IrB⁻ was found to be $1\sigma^2 1\pi^4 2\sigma^2 1\delta^3 3\sigma^2$ with a ${}^2\Delta_{5/2}$ ground state. The ${}^2\Sigma^+$ state with a $1\sigma^2 1\pi^4 2\sigma^2 1\delta^4 3\sigma^1$ electron configuration was calculated to be 0.237 eV higher in energy than the ${}^2\Delta$ state. This energy ordering is different from that of RhB⁻, for which the ${}^2\Sigma^+$ state is the ground state.²⁶ Detaching an electron from the 3σ orbital of the anion ground state yields either a ${}^3\Delta$ or ${}^1\Delta$ final state for IrB, while detaching an electron from the 1δ orbital of the anion ground state gives the ${}^3\Sigma^-$ or the ${}^1\Gamma$ excited state of IrB. Our calculated lowest energy state for IrB is the ${}^3\Delta$ state, consistent with the previous studies.^{13,15} The ${}^3\Delta$ state splits into three spin–orbit (SO) terms, ${}^3\Delta_3$, ${}^3\Delta_2$, and ${}^3\Delta_1$, but the splitting could not be computed at the level of



FIG. 5. Photoelectron image and spectrum of AuB^- at 1.4058 eV. The double arrow below the images indicates the laser polarization. The vertical lines represent vibrational structures.

theory used in the current work. Although it is not accessible from one-electron detachment, there is a $^{1}\Sigma^{+}$ excited state with an electron configuration of $1\sigma^{2}1\pi^{4}2\sigma^{2}1\delta^{4}3\sigma^{0}$, which corresponds to the ground state of RhB.²⁶ Our calculations indicate that the $^{1}\Sigma^{+}$ and the $^{1}\Delta$ excited states are 0.176 eV and 0.231 eV higher in energy than the $^{3}\Delta$ ground state, respectively. The $^{3}\Sigma^{-}$ and the $^{1}\Gamma$ excited states are computed to be 1.341 eV and 2.407 eV higher in energy than the ground state, respectively, and they are not accessible in the current experiment.

Our computed ADE to the ${}^{3}\Delta$ state is 1.957 eV (Table I), which is also the theoretical EA for IrB without considering the SO effects. The calculated bond length of IrB⁻ is 1.808 Å, while that for neutral IrB is 1.763 Å for the ${}^{3}\Delta$ state and 1.722 Å for the ${}^{1}\Sigma^{+}$ state, consistent with the antibonding characters of the 3 σ orbital. The computed vibrational frequency is 882 cm⁻¹ for the ${}^{2}\Delta$ ground state of the ${}^{193}\text{Ir}{}^{11}\text{B}^{-}$ anion, 942 cm⁻¹ for the ${}^{3}\Delta$ ground state of neutral ${}^{193}\text{Ir}{}^{11}\text{B}$, and 994 cm⁻¹ for the ${}^{1}\Sigma^{+}$ excited state of neutral ${}^{193}\text{Ir}{}^{11}\text{B}$. The bond length and vibrational frequency for the ${}^{1}\Delta$ state of neutral ${}^{193}\text{Ir}{}^{11}\text{B}$ could not be computed at the current level of theory.

B. PtB⁻

The PtB⁻ anion has one more electron than IrB⁻, and it is found to have a closed-shell electron configuration, $1\sigma^2 1\pi^4 2\sigma^2 1\delta^4 3\sigma^2$, with a ${}^{1}\Sigma^{+}$ ground state. Detaching an electron from the 3σ highest occupied molecular orbital (HOMO) gives rise to the ${}^{2}\Sigma^{+}$ ground state of neutral PtB. The calculated detachment energy or EA of PtB is 2.097 eV (Table II). Higher detachment channels were not computed because they were not accessible in the current experiment. The calculated bond lengths for the ground states of PtB⁻ and PtB are 1.799 Å and 1.755 Å, respectively. The vibrational frequency for the ${}^{195}\text{Pt}^{10}\text{B}^{-}$ anion was calculated to be 913 cm⁻¹, while that for neutral ${}^{195}\text{Pt}^{10}\text{B}$ was computed to be 984 cm⁻¹ (Table II).

C. AuB⁻

The AuB⁻ anion has one more electron than PtB⁻, and it has an electron configuration of $1\sigma^2 1\pi^4 2\sigma^2 1\delta^4 3\sigma^2 2\pi^1$ with a ² Π ground

state. The additional electron occupies the antibonding 2π LUMO of the neutral AuB. Detachment of the electron from the 2π orbital in AuB⁻ yields the ${}^{1}\Sigma^{+}$ ground state of AuB. The EA of AuB was computed to be 0.764 eV (Table II). The bond lengths for the anion and neutral were calculated to be 1.949 Å and 1.906 Å, respectively. The vibrational frequency was computed to be 614 cm⁻¹ for the Au¹⁰B⁻ anion and 710 cm⁻¹ for neutral Au¹⁰B (Table II).

VI. SPECTRAL ASSIGNMENTS AND COMPARISON BETWEEN EXPERIMENT AND THEORY

A. IrB⁻

The electronic structure of IrB is complicated because of the SO-splitting in its open-shell ground state $({}^{3}\Delta_{3,2,1})$ and the fact that the ${}^{1}\Delta$ excited state is close in energy to the triplet ground state. Vibrational hot bands added further spectral congestions, resulting in the somewhat complicated PE spectra shown in Fig. 2. The observed detachment transitions are represented in the energy level diagram in Fig. 6, and the detailed assignments and comparison with theory are given in Table I.

Peak \bar{X} represents the 0–0 transition to the ${}^{3}\Delta_{3}$ ground state. The EA for IrB (1.995 eV) determined from peak X agrees well with the calculated value (1.957 eV, Table I). Peak A is assigned to the transition to the ${}^{1}\Delta$ excited state of IrB. The calculated binding energy (2.188 eV) for the ${}^{1}\Delta$ state is in good accord with the experimental data (2.116 eV, Table I). This assignment yields an excitation energy of 976 cm⁻¹ for the ${}^{1}\Delta$ state relative to the ${}^{3}\Delta_{3}$ ground state, compared to our computed excitation energy of 1863 cm⁻¹ (0.231 eV) at the TD-B3LYP level and 2283 cm⁻¹ (0.283 eV) at the MRCI level (Table I). In a previous LIF study, a band system to the ${}^{1}\Delta$ state was observed, but its energy relative to the ground state was not observed and a computed value of 1500 cm⁻¹ was given instead.¹⁸ These relatively large discrepancies between the theoretical values and the experimental data are likely due to strong electron



FIG. 6. Energy level diagram and the corresponding transitions observed in the experiment for $\mbox{IrB}^-.$

correlation effects in this system. Peak B is assigned to the transition to the ${}^{3}\Delta_{2}$ state. Its separation from peak X is 2900 cm⁻¹, slightly smaller than the computed value at the MRCI level (3428 cm⁻¹, Table I). The β values for the X, A, and B peaks display similar trends as a function of electron kinetic energies (Fig. 3), in agreement with the fact that all three states are produced from electron detachment from the same MO. Apparently, the ${}^{3}\Delta_{1}$ state is too high in energy and not accessible in the current experiment. The remaining peaks are due to vibrational excitations and hot band transitions (Fig. 6).

A short vibrational progression was observed for each of the three final electronic states, as indicated by the vertical lines in Fig. 2(c) for the ${}^{3}\Delta_{3}$ state, Fig. 2(d) for the ${}^{1}\Delta$ state, and Fig. 2(f) for the ${}^{3}\Delta_{2}$ state. Because all three electronic states are originated from electron detachment from the slightly antibonding 3σ orbital, the measured vibrational frequencies for these states are similar and close to the computed frequency of 942 cm⁻¹ (Table I). Our measured vibrational frequency (925 cm⁻¹) for the ${}^{3}\Delta_{3}$ state of 193 Ir 11 B is consistent with the previously reported value (909 cm^{-1}),¹⁸ considering the relatively large error bar in the current measurement. Several hot band transitions were observed, involving v = 1 and 2 of the anion and different final neutral states, as shown schematically in Fig. 6. The hot band transitions yielded an average experimental vibrational frequency for the anion as 844 cm⁻¹, in good agreement with the computed frequency of 882 cm^{-1} (Table I). The smaller anion vibrational frequency in comparison with that of the neutral ground state is consistent with the antibonding nature of the 3σ orbital.

B. PtB⁻

The calculated ADE for PtB⁻ is 2.097 eV, which agrees well with the experimental value (2.153 eV), as shown in Table II. The observed vibrational progression yielded a vibrational frequency of 974 cm⁻¹ for the ground state of the ¹⁹⁵Pt¹⁰B isotopomer probed experimentally, in excellent agreement with the calculated frequency of 984 cm⁻¹ (Table II). The previous LIF experiment yielded a vibrational frequency of 903.6 cm⁻¹ for the ¹⁹⁵Pt¹¹B isotopomer, in line with the expected isotope shift.²⁰ Peak *hb*1 represents the transition from the first vibrational excited state of the anion to the neutral ground state, yielding an experimental frequency of 829 cm⁻¹ for the ¹⁹⁵Pt¹⁰B⁻ anion, compared with the calculated vibrational frequency of 913 cm^{-1} (Table II). The increase in the vibrational frequency upon photodetachment is consistent with the antibonding nature of the 3σ HOMO in PtB⁻. The β values for the X peak of PtB⁻ are similar to those of the detachment features of IrB⁻ (Fig. 3), confirming the fact that electron detachment takes place from the same orbital in the two systems.

C. AuB⁻

The experimental ADE of 0.877 eV for AuB⁻ is relatively low, in agreement with the computed value of 0.764 eV (Table II). The observed vibrational progression yielded a frequency of 704 cm⁻¹, agreeing well with the calculated frequency of 710 cm⁻¹. The poor signal-to-noise ratios of the PE spectrum prevented us from resolving any hot band transitions to yield an experimental vibrational frequency for the anion. The computed frequency of 614 cm⁻¹ **TABLE III.** The calculated bond lengths (r_0) for IrB, PtB, and AuB compared with the respective triple bond lengths computed using Pyykko's self-consistent covalent radii ($r_{M\equiv\equiv B}$). The theoretical values for the bond dissociation energies D_0 (in eV) are also given in comparison with the experimental data.

	IrB ($^{3}\Delta$)	PtB ($^{2}\Sigma^{+}$)	AuB $(^{1}\Sigma^{+})$
r ₀ (Å)	1.763 ^a	1.755 ^b	1.906
$r_{\mathrm{M}\equiv\mathrm{B}}$ (Å) ^c	1.80	1.83	1.96
D_0 (Expt.)	4.928 ^d	5.235 ^d	3.812 ^e
D_0 (Theo.)	5.085	5.668	3.734

^aExperimental bond length 1.7675 Å from Ref. 13.

^bExperimental bond length 1.741 Å from Ref. 20.

^cFrom Ref. 50.

^dFrom Ref. 25.

^eFrom Ref. 6.

for $Au^{10}B^-$ is significantly smaller than that for neutral $Au^{10}B$, consistent with the strong antibonding nature of the 2π LUMO of AuB.

D. The bond dissociation energies of the MB⁻ anions

In Table III, the experimental bond dissociation energies of the three MB molecules are compared with the current calculations. In the cases of IrB and AuB, the calculated D_0 values are in good agreement with the previous experimental data. However, the current level of theory seemed to have overestimated the D_0 value for PtB.

More interestingly, we can now obtain the experimental bond dissociation energies for IrB⁻, PtB⁻, and AuB⁻ using our measured EA values and the known EAs for the atoms and the D_0 of the neutral MB species. Because there are two possible dissociation limits, MB⁻ \rightarrow M⁻ + B or M + B⁻, two possible D_0 (MB⁻) values can be obtained using the following relationships:

and

$$D_0(M-B^-) = EA(MB) + D_0(MB) - EA(B).$$

 $D_0(M^--B) = EA(MB) + D_0(MB) - EA(M)$

The results are given in Table IV, in comparison with our calculated values. The theoretical data are in good agreement with the experimentally deduced values. Again we found that the D_0 values for the PtB⁻ anions are slightly overestimated, similar to the case for the

TABLE IV. Experimentally deduced bond dissociation energies (in eV) of IrB⁻, PtB⁻, and AuB⁻ compared with the theoretical results.^a

	Ir	Pt	Au
$D_0(M^B)$ (Expt.)	5.359 ^a	5.263	2.380
$D_0(M^B)$ (Theo.)	5.539	5.698	2.144
$D_0(M-B^-)$ (Expt.)	6.643	7.108	4.409
$D_0(M-B^-)$ (Theo.)	6.845	7.568	4.187

^aThe electron affinities for the atoms are from Ref. 52.

PtB neutral (Table III). It is interesting to note that the $D_0(MB^-)$ values are all larger than the respective $D_0(MB)$ values (Table III) because the EAs of the atoms are all smaller than the EAs of the MB molecules.

VII. DISCUSSION: THE CHEMICAL BONDING IN DIATOMIC METAL BORIDES

The calculated bond lengths for the three MB diatomic boride molecules are remarkably short and are all shorter than the respective triple bond lengths based on Pyykko's self-consistent triplebond covalent radii,⁵⁰ as shown in Table III. The calculated bond length for IrB (1.763 Å) agrees well with the experimental value (1.7675 Å), whereas the experimental bond length of PtB (1.741 Å) is slightly shorter than the calculated value (1.755 Å). There is no experimental measurement for the bond length of AuB, but the calculated value should be reliable. The valence MO diagrams and occupancies of the three MB species are shown in Fig. 7, which is similar to that of RhB (Fig. 1). The 1σ MO is a bonding orbital between the M $5d_{z^2}$ and the B 2s atomic orbitals with small contributions from the B_{2p_z} orbital (Table V). The 1π MOs are bonding orbitals between the M $5d_{xz}/5d_{yz}$ and the B $2p_x/2p_y$ atomic orbitals. The 2σ MO is a bonding orbital between the M $5d_{r^2}$ and the B sp hybridized orbitals. The 1δ MOs are of pure M 5d characters, while the 3σ MO is a weak antibonding orbital mainly between the M 6s and the B sp hybridized orbitals. While the major contribution to the 3σ MO is the M 6s orbital, there is a significant contribution from the M $6p_z$ orbital (Table V), which is out of phase with the B sp orbital for the weak antibonding interaction. Not shown is the 2π antibonding orbital, which is occupied by the extra electron in AuB⁻ (Sec. V C). The detailed orbital compositions based on the closed shell species [IrB (${}^{1}\Sigma^{+}$), PtB⁻ (${}^{1}\Sigma^{+}$), and AuB (${}^{1}\Sigma^{+}$)] are given in Table V.

A. IrB

Unlike the isoelectronic and quadruply bonded Rh \equiv B ($^{1}\Sigma^{+}$), IrB has a triplet ground state $({}^{3}\Delta)$ with the promotion of a 1 δ electron to the 3σ antibonding orbital [Fig. 7(a)], which weakens the quadruple bond. This difference in their electronic structure is due to the relativistic effects, as also reflected in the different atomic configurations of Rh and Ir: The Rh atom has a [Kr]4d⁸5s¹ ground state configuration, while Ir has a [Xe]4f¹⁴5d⁷6s² configuration. The strong relativistic effects tend to stabilize the 6s orbital more than the 5d orbitals in Ir,⁵¹ hence also stabilizing the 3σ MO in IrB relative to that in RhB. The EA of IrB (1.995 eV) is much higher than that of RhB (0.961 eV), consistent with the stabilization of the 3σ MO in IrB. We computed the differences in orbital energies between the 3σ SOMO and the 1δ HOMO for the $^{2}\Sigma^{+}$ state in RhB⁻ and IrB⁻. The SOMO-HOMO gap in RhB⁻ is 2.107 eV, while that in IrB⁻ is only 0.454 eV. This explains why in neutral IrB the ${}^{3}\Delta$ state is lower in energy than the ${}^{1}\Sigma^{+}$ state due to the small 1 δ to 3 σ promotion energy.

Although not accessible from one-electron detachment from the ${}^{2}\Delta_{5/2}$ ground state of the anion, the ${}^{1}\Sigma^{+}$ state of IrB is calculated to be only 0.176 eV higher in energy than the ${}^{3}\Delta_{3}$ ground state. The ${}^{1}\Sigma^{+}$ excited state of IrB, in which the 1 δ HOMO is fully occupied like in Rh \equiv B, is calculated to have an extremely short bond length



FIG. 7. Schematics of the MO diagrams for the transition metal MB diatomics (left) and the MO occupations for (a) IrB, (b) PtB, and (c) AuB.

(1.722 Å) and a very high vibrational frequency (994 cm⁻¹), consistent with its true quadruple bond nature. Hence, the bond order of the ${}^{3}\Delta$ ground state of IrB can be considered to be three and half, consistent with the slightly smaller D_{0} value of IrB relative to that of the quadruply bonded Rh \equiv B. The bond order of IrB agrees well with the fact that its bond length is shorter than the triple bond length (Table III). It is interesting to note that the π orbital compositions in IrB (Table V) are identical to those in RhB (Fig. 1), whereas the two σ orbitals in IrB are slightly more covalent than those in RhB. It is clear that the 1 σ MO is a strong bonding orbital, not a B 2s lone pair, as generally assumed previously.

B. PtB

The PtB molecule has one more electron than IrB with a configuration of $1\sigma^2 1\pi^4 2\sigma^2 1\delta^4 3\sigma^1$ [Fig. 7(b)]. Because the 1 δ MO is nonbonding, the bond order of PtB is the same as that of IrB. However, the D_0 value of PtB (5.235 eV) is substantially larger than that of IrB (4.928 eV) and is close to that of the quadruply bonded Rh \equiv B (5.252 eV).²⁵ The stronger bond in PtB is also reflected by its short bond length (Table III) and large vibrational frequency: 974 cm⁻¹ for ¹⁹⁵Pt¹⁰B from the current experiment (Table II) or 903.60 cm⁻¹ for ¹⁹⁵Pt¹¹B from the previous LIF study.²⁰ The strong PtB bond can be glimpsed from its valence MO compositions (Table V). Both the 1 σ and 2 σ MOs have strong covalent bond characters with substantial contributions from the Pt 6s orbital. The enhanced 6s participation in the σ bonds is again due to the greater relativistic stabilization of the 6s orbital in Pt compared to Ir. The relativistic contraction of the 6s shell displays a maximum for Au, while that of Pt is close to Au, but much greater than that of Ir.⁵¹ The increased EA of PtB (2.153 eV) relative to that of IrB (1.995 eV) is consistent with the increased stability of the 6s orbital in Pt compared to that in Ir.

C. AuB

The AuB molecule has a closed-shell electronic structure with the antibonding 3σ orbital fully occupied [Fig. 7(c)]. The fully occupied 3o antibonding orbital significantly weakens the bond in AuB, yielding an overall bond order of three. The bond dissociation energy of AuB (3.773 eV), measured from a previous Knudsen cell experiment,^o is smaller than that of PtB, but it is still quite substantial, in accord with the multiple bonding nature in AuB. In fact, our calculated AuB bond length (1.906 Å) is shorter than the triple bond length estimated from Pyykko's self-consistent covalent radii for the AuB triple bond (1.96 Å), as shown in Table III. A previous calculation gave a D_0 value of 3.52 eV and a bond length of 1.931 Å for AuB,⁷ mainly due to the strong relativistic effects of Au. The previous calculation showed that the relativistic effects increased the D₀ of AuB from 1.26 eV (non-relativistic) to 3.52 eV and reduced its bond length from 2.256 Å to 1.931 Å. In the current study, we experimentally measured the vibrational frequency for Au¹⁰B as

	3σ	1δ	2σ	1π	1σ
IrB	66%6s + 8%6pz+ 13%2pz+3%2s	$100\%5d_x2_{-y^2}/5d_{xy}$	$\frac{45\%5d_{z^2}+39\%2s+}{12\%2p_z}$	$83\%5d_{xz}/5d_{yz}+16\%2p_x/p_y$	$\frac{37\%5d_{z^2}+5\%6s+}{50\%2s+4\%2p_z}$
PtB ⁻	$54\%6s + 6\%6p_z + 24\%2p_z + 11\%2s$	$100\%5d_x2_{-y}2/5d_{xy}$	$\begin{array}{r} 47\%5d_{z}2{+}10\%6s + \\ 31\%2s + 10\%2p_{z} \end{array}$	$89\%5d_{xz}/5d_{yz}$ +11%2p _x /p _y	38%5dz2+8%6s + 45%2s + 4%2pz
AuB	49%6s + 2%6pz+ 19%2pz+29%2s	$100\%5d_x2_{-y}2/5d_{xy}$	$\frac{48\%5d_{z}2+15\%6s+}{34\%2s+1\%2p_{z}}$	$96\%5d_{xz}/5d_{yz} + 4\%2p_x/p_y$	45%5d _z 2+8%6s + 39%2s + 5%2p _z

TABLE V. The valence orbital compositions for the closed shell IrB ($^{1}\Sigma^{+}$), PtB⁻ ($^{1}\Sigma^{+}$), and AuB ($^{1}\Sigma^{+}$).

ARTICLE

704 cm⁻¹ for the first time, which is in good agreement with the computed value (710 cm⁻¹) (Table II). The Au 6s orbital is involved even more in the 1 σ and 2 σ bonding orbitals than those in PtB (Table V). The orbital decomposition analyses show that the π bonds are relatively weak with only a 4% contribution from the B 2p_x/2p_y orbitals. Therefore, AuB can be viewed as possessing a weak triple bond.

VIII. CONCLUSION

We have used high resolution photoelectron imaging and theoretical calculations to examine the nature of the chemical bonding in three late 5d transition metal diatomic boride species, IrB, PtB, and AuB. Vibrationally resolved photoelectron spectra were obtained for the corresponding anions, and the electron affinities of the three species were measured for the first time. Three electronic states were observed for IrB (X³ Δ_3 , ³ Δ_2 , and ¹ Δ_2), whereas only the ground state was observed for PtB $(X^2\Sigma^{\scriptscriptstyle +})$ and AuB $(X^1\Sigma^{\scriptscriptstyle +}).$ Theoretical results show that IrB, PtB, and AuB all have multiple bonding characters. In the ground states of IrB and PtB, the antibonding 3σ orbitals are singly occupied, resulting in an overall bond order between a triple bond and a quadruple bond. The antibonding 30 orbital is fully occupied in AuB, giving rise to a weak triple bond. The current study provides new insight into the nature of the strong bonding interactions in diatomic species between the late 5d transition metals and boron.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (Grant No. CHE-1763380). We would like to thank one of the reviewers who made the suggestion to deduce the bond dissociation energies for the anions.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

¹H.-Y. Chung, M. B. Weinberger, J. B. Levine, A. Kavner, J.-M. Yang, S. H. Tolbert, and R. B. Kaner, Science **316**, 436–439 (2007).

²J. V. Rau and A. Latini, Chem. Mater. 21, 1407–1409 (2009).

³A. G. Kvashnin, Z. Allahyari, and A. R. Oganov, J. Appl. Phys. **126**, 040901 (2019).

⁵P. J. Robinson, G. Liu, S. Ciborowski, C. Martinez-Martinez, J. R. Chamorro, X. Zhang, T. M. McQueen, K. H. Bowen, and A. N. Alexandrova, Chem. Mater. 29, 9892–9896 (2017).

⁶K. A. Gingerich, J. Chem. Phys. 54, 2646–2650 (1971).

⁷M. Barysz and M. Urban, Adv. Quantum Chem. 28, 257–272 (1997).

⁸Z. Wu, J. Mol. Struct.: THEOCHEM 728, 167-172 (2005).

- ⁹P. K. Chowdhury and W. J. Balfour, J. Chem. Phys. **124**, 216101 (2006).
- ¹⁰P. K. Chowdhury and W. J. Balfour, Mol. Phys. **105**, 1619–1624 (2007).
- ¹¹A. C. Borin and J. P. Gobbo, J. Phys. Chem. A **112**, 4394–4398 (2008).
- ¹²D. Tzeli and A. Mavridis, J. Chem. Phys. **128**, 034309 (2008).
- ¹³J. Ye, H. F. Pang, A. M.-Y. Wong, J. W.-H. Leung, and A. S.-C. Cheung, J. Chem. Phys. **128**, 154321 (2008).

- ¹⁴W. J. Balfour, P. K. Chowdhury, and R. Li, Chem. Phys. Lett. **463**, 25–28 (2008).
- ¹⁵V. Kalamse, S. Gaikwad, and A. Chaudhari, Bull. Mater. Sci. 33, 233–238 (2010).
- ¹⁶J.-f. Zhen, L. Wang, C.-b. Qin, Q. Zhang, and Y. Chen, Chin. J. Chem. Phys. 23, 626–629 (2010).
- ¹⁷Y. W. Ng, H. F. Pang, and A. S.-C. Cheung, J. Chem. Phys. **135**, 204308 (2011).
 ¹⁸H. F. Pang, Y. W. Ng, Y. Xia, and A. S.-C. Cheung, Chem. Phys. Lett. **501**, 257–262 (2011).
- ¹⁹A. C. Borin and J. P. Gobbo, Int. J. Quantum Chem. **111**, 3362–3370 (2011).
- ²⁰Y. W. Ng, Y. S. Wong, H. F. Pang, and A. S.-C. Cheung, J. Chem. Phys. 137, 124302 (2012).

²¹ N. Wang, Y. W. Ng, and A. S.-C. Cheung, Chem. Phys. Lett. 547, 21–23 (2012).
 ²² A. C. Borin and J. P. Bobbo, J. Mol. Model. 20, 2285–3370 (2011).

- ²³E. S. Goudreau, A. G. Adam, D. W. Tokaryk, and C. Linton, J. Mol. Spectrosc. 314, 13–18 (2015).
- ²⁴ J. M. Dore, A. G. Adam, D. W. Tokaryk, and C. Linton, J. Mol. Spectrosc. 360, 44–48 (2019).
- ²⁵D. M. Merriles, E. Tieu, and M. D. Morse, J. Chem. Phys. 151, 044302 (2019).
 ²⁶L. F. Cheung, T.-T. Chen, G. S. Kocheril, W.-J. Chen, J. Czekner, and L.-S.
- Wang, J. Phys. Chem. Lett. 11, 659–663 (2020).
 ²⁷H.-J. Zhai, L.-S. Wang, A. N. Alexandrova, and A. I. Boldyrev, J. Chem. Phys. 117, 7917–7924 (2002).
- ²⁸ A. P. Sergeeva, B. B. Averkiev, H.-J. Zhai, A. I. Boldyrev, and L.-S. Wang, J. Chem. Phys. **134**, 224304 (2011).
- ²⁹Z. A. Piazza, W.-L. Li, C. Romanescu, A. P. Sergeeva, L.-S. Wang, and A. I. Boldyrev, J. Chem. Phys. **136**, 104310 (2012).
- ³⁰ A. P. Sergeeva, I. A. Popov, Z. A. Piazza, W.-L. Li, C. Romanescu, L.-S. Wang, and A. I. Boldyrev, Acc. Chem. Res. 47, 1349–1358 (2014).
- ³¹L.-S. Wang, Int. Rev. Phys. Chem. 35, 69–142 (2016).
- ³²W. L. Li, X. Chen, T. Jian, T. T. Chen, J. Li, and L. S. Wang, Nat. Rev. Chem. 1, 0071 (2017).
- ³³T. Jian, X. Chen, S.-D. Li, A. I. Boldyrev, J. Li, and L.-S. Wang, Chem. Soc. Rev. 48, 3550–3591 (2019).
- ³⁴J. Czekner, L. F. Cheung, G. S. Kocheril, M. Kulichenko, A. I. Boldyrev, and L. S. Wang, Angew. Chem., Int. Ed. 58, 8877–8881 (2019).
- ³⁵T.-T. Chen, W.-L. Li, W.-J. Chen, J. Li, and L.-S. Wang, Chem. Commun. 55, 7864–7867 (2019).
- ³⁶L. F. Cheung, G. S. Kocheril, J. Czekner, and L.-S. Wang, J. Am. Chem. Soc. **142**, 3356–3360 (2020).
- ³⁷I. León, Z. Yang, H.-T. Liu, and L.-S. Wang, Rev. Sci. Instrum. **85**, 083106 (2014).
- ³⁸I. León, Z. Yang, and L.-S. Wang, J. Chem. Phys. 138, 184304 (2013).
- ³⁹B. Dick, Phys. Chem. Chem. Phys. 16, 570–580 (2014).
- ⁴⁰ A. Sanov and R. Mabbs, Int. Rev. Phys. Chem. 27, 53–85 (2008).
- ⁴¹S. Grimme, J. Chem. Phys. 124, 034108 (2006).
- 42 T. H. Dunning, J. Chem. Phys. 90, 1007–1023 (1989).

⁴³D. Figgen, G. Rauhut, M. Dolg, and H. Stoll, Chem. Phys. 311, 227–244 (2005).

⁴⁴D. Figgen, K. A. Peterson, M. Dolg, and H. Stoll, J. Chem. Phys. **130**, 164108 (2009).

- ⁴⁵K. A. Peterson and C. Puzzarini, Theor. Chem. Acc. 114, 283–296 (2005).
- ⁴⁶A. D. Becke, J. Chem. Phys. **98**, 5648–5652 (1993).
- ⁴⁷M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. L. Martin, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin,
- K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg,

⁴R. B. Kaner, J. J. Gilman, and S. H. Tolbert, Science 308, 1268–1269 (2005).

S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision C.1 (Gaussian, Inc., Wallingford, CT, 2009).

⁴⁸H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2015.1, see http://www.molpro.net.

- ⁴⁹T. Lu and F. Chen, J. Comput. Chem. 33, 580–592 (2012).
 ⁵⁰P. Pyykkö, J. Phys. Chem. A 119, 2326–2337 (2015).
- ⁵¹ P. Pyykko, Chem. Rev. 88, 563–594 (1988).

⁵²T. Andersen, H. K. Haugen, and H. Hotop, J. Phys. Chem. Ref. Data 28, 1511 (1999).